

1 Attorney Docket No. 83346

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3 MOLYBDENUM-COPPER COMPOSITE MATERIAL

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5 STATEMENT OF GOVERNMENT INTEREST

6 The invention described herein may be manufactured and used  
7 by or for the Government of the United States of America for  
8 governmental purposes without the payment of any royalties  
9 thereon or therefore.

10

11 CROSS-REFERENCE TO RELATED PATENT APPLICATIONS

12 This patent application is co-pending with one related  
13 patent application entitled STAINLESS STEEL-COPPER COMPOSITE  
14 MATERIAL (Attorney Docket No. 83344), by the same inventor as  
15 this application.

16

17 BACKGROUND OF THE INVENTION

18 (1) Field of the Invention

19 The present invention relates to a molybdenum-copper  
20 composite material which may be used to manufacture parts and  
21 tools requiring working temperatures up to 1,000 degrees  
22 Centigrade and to a method of making the composite material to a  
23 desired form using either cold pressing or selective laser  
24 sintering.

1 (2) Description of the Prior Art

2 Sintered copper alloys are known in the art. For example,  
3 U.S. Patent No. 4,935,056 to Miyasaka illustrates a wear-  
4 resistant copper-base sintered oil containing bearing material  
5 having a structure which contains 2 to 11% by weight of tin and  
6 1 to 20% by weight of cobalt and further includes 2 to 15% by  
7 weight of at least one of molybdenum disulfide, graphite and  
8 lead serving as solid lubricants. Dispersed throughout the  
9 structure is cobalt at an average particle size equal to or less  
10 than 20 microns.

11 U.S. Patent No. 5,824,922 to Aonuma illustrates a wear-  
12 resistant sintered alloy having a general composition consisting  
13 essentially of in weight ratio 0.736 to 9.65% nickel, 0.736 to  
14 2.895% copper, 0.294 to 0.965% molybdenum, 0.12 to 6.25%  
15 chromium, and 0.508 to 2.0% carbon with the balance being iron,  
16 and inevitable impurities. The alloy has a metallic structure  
17 in which there are dispersed (1) a martensite, (2) a bainite  
18 having a nucleus of sorbite and/or upper bainite surrounding  
19 said nucleus, (3) an austenite having a high nickel  
20 concentration, and (4) a hard phase surrounding with a ferrite  
21 having a high chromium concentration and composed mainly of a  
22 chromium carbide.

23 U.S. Patent No. 5,870,663 to Stucker et al. illustrates a  
24 wear-resistant Zirconium-DiBoride ( $ZrB_2$ ) -Copper Alloy composite

1 electrode. Wherein the first furnace cycle produces a sintered  
2 shaped form which is about 30 vol.% to about 70 vol.% occupied  
3 by sintered ZrB<sub>2</sub>. Wherein the first furnace cycle comprises  
4 heating the desired form room temperature to about 1,300 degrees  
5 C to about 1,900 degrees C. Wherein the sintered ZrB<sub>2</sub> is then  
6 contacted with a copper alloy comprised of up to about 3 wt.%  
7 boron and up to about 10 wt.% nickel. Wherein a second furnace  
8 cycles is used to heat the sintered ZrB<sub>2</sub> and copper alloy above  
9 the melting point of the copper alloy to infiltrate the ZrB<sub>2</sub> with  
10 copper alloy to form a ZrB<sub>2</sub>/copper alloy composite electrode.

11 Despite the existence of these materials, there exists a  
12 need for a material that offers the ability to create tools and  
13 prototype parts requiring working temperatures up to 1000  
14 degrees Centigrade.

15

16 SUMMARY OF THE INVENTION

17 Accordingly, it is an object of the present invention to  
18 provide a composite material that offers the ability to create  
19 tools and prototype parts requiring working temperatures up to  
20 1000 degrees Centigrade.

21 It is a further object of the present invention to provide  
22 a composite material as above which has a low coefficient of  
23 thermal expansion.

1        It is still a further object of the present invention to  
2 provide a method for manufacturing the above composite material.

3        The foregoing objects are attained by the composite  
4 material and method of the present invention.

5        In accordance with the present invention, a composite  
6 material is provided which has a molybdenum particulate and an  
7 oxygen free copper matrix. The molybdenum is preferably present  
8 in an amount of 35 - 65 vol% with the balance being of oxygen  
9 free copper.

10       Also, in accordance with the present invention, a method  
11 for manufacturing a molybdenum-copper composite material broadly  
12 comprises forming a mixture of molybdenum, phenolic, and wax,  
13 forming the mixture into a green form using either a selective  
14 laser sintering process or a cold pressing process, placing the  
15 green form and oxygen free copper into the furnace adjacent to  
16 the green form, and subjecting the green form and the oxygen  
17 free copper to a furnace cycle. During the furnace cycle the  
18 wax and phenolic thermoset resin is vaporized and the molybdenum  
19 is sintered. Additionally, the sintered molybdenum substrate,  
20 which is contacted with copper, is heated above the melting  
21 point of the copper which causes the copper to infiltrate the  
22 molybdenum substrate, forming the molybdenum-copper composite  
23 part.

1       Other details of the molybdenum-copper composite material,  
2   as well as other objects and advantages attendant thereto, are  
3   set forth in the following detailed description.

4

5                   DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

6       The molybdenum-copper composite material is a particulate  
7   composite created from molybdenum, phenolic, wax, and oxygen  
8   free copper. The material is manufactured using an indirect  
9   selective laser sintering (SLS) process, where a  
10   molybdenum/phenolic/wax powder mixture is initially sintered  
11   into a green form. Upon completion of sintering, the green form  
12   is placed through a furnace cycle for de-binding and  
13   infiltration of the oxygen free copper.

14       Molybdenum is a hard, malleable, ductile, high melting,  
15   silver white metal with a body-centered cubic crystalline  
16   structure. It is a metallic element which is most frequently  
17   used as an alloying addition in alloy and stainless steels. Its  
18   alloying versatility is unmatched because its addition enhances  
19   strength, hardenability, weldability, toughness, elevated  
20   temperature strength and corrosion resistance. Alloys  
21   containing molybdenum are used in making high-speed cutting  
22   tools, aircraft parts, and forged automobile parts. Because it  
23   retains its strength and structure at very high temperatures, it  
24   has found use in certain critical rocket and missile parts.

- 1 Molybdenum is not attacked by air at ordinary temperature, but
- 2 at elevated temperatures, it oxidizes to form molybdenum oxide.
- 3 Molybdenum melts at about 2617 degrees Centigrade.
- 4 The desired material properties of molybdenum is as
- 5 follows:

Property	Molybdenum
Density (g/cm <sup>3</sup> )	10.22
Tensile Yield Strength (MPa)	550
Ultimate Tensile Strength (MPa)	650
Modulus of Elasticity (GPa)	324.8
Hardness (Vickers, Gpa)	200
Coefficient of Thermal Expansion (m/m/°C)	5.04E-6
Thermal Conductivity (W/mK)	146
Melting point (°C)	2,614

- 6
- 7 Phenolic is a thermoset synthetic resin generally employed
- 8 as a molding material for the making of mechanical and
- 9 electrical parts. There are hundreds of different phenolic
- 10 molding compounds and in general they have a balance of
- 11 moderately good mechanical and electrical properties and are
- 12 generally suitable in temperatures up to 160 degrees Centigrade.
- 13 The resins are marketed usually in a granular form, partly
- 14 polymerized for molding under heat and pressure which completes
- 15 the polymerization process, making the product infusible and
- 16 relatively insoluble.

1        The desired material properties of the phenolic thermoset  
2    resin is as follows:

Property	Phenolic
Density (g/cm <sup>3</sup> )	1.1 - 1.3
Tensile Yield Strength (MPa)	52.0
Ultimate Tensile Strength (MPa)	60.0
Ultimate Compressive Strength (MPa)	140.0
Modulus of Elasticity (GPa)	6.0
Hardness	130.0, Rockwell M
Coefficient of Thermal Expansion (m/m/°C)	77.0E-6
Thermal Conductivity (W/mK)	0.2
Electrical Resistivity (Ohm-cm)	5.0E11
Melting point (°C)	---
Maximum Service Temperature (°C)	160

3  
4        Oxygen-free high conductivity copper (C10100) is produced  
5    by the direct conversion of selected refined cathodes and  
6    castings under carefully controlled conditions to prevent any  
7    contamination of the pure oxygen-free metal during processing.  
8       The method of producing oxygen-free high conductivity copper  
9    insures extra high grade of metal with a copper content of 99.9%  
10   by weight. With so small a content of extraneous elements, the  
11   inherent properties of elemental copper are brought forth to a  
12   high degree. Characteristics are high ductility, high  
13   electrical and thermal conductivity, high impact strength, good  
14   creep resistance, ease of welding, and low volatility under high

1 vacuum. Some typical uses for copper alloy C10100 in the  
2 electrical and electronic industries are bus bars, bus  
3 conductors, wave guides, hollow conductors, lead-in wires and  
4 anodes for vacuum tubes, glass to metal seals and others.

5 The desired material properties of the oxygen free copper  
6 is as follows:

Property	O <sub>2</sub> Free Cu
Density (g/cm <sup>3</sup> )	8.96
Tensile Yield Strength (MPa)	33.3
Ultimate Tensile Strength (MPa)	210
Modulus of Elasticity (GPa)	110
Hardness (Vickers, Gpa)	49
Coefficient of Thermal Expansion (m/m/°C)	17.64E-6
Thermal Conductivity (W/mK)	346
Melting point (°C)	1,083

7

8 To form the composite material of the present invention, a  
9 mixture of molybdenum, phenolic, and wax is formed. The mixture  
10 may be shaped into the form of a part or component to be  
11 produced. The mixing of molybdenum particles with wax and  
12 phenolic thermoset resin particles should be done in a way such  
13 that the particles are evenly dispersed. The preferred  
14 molybdenum, wax, and phenolic thermoset resin particle size for  
15 the selective laser sintering shaping method should be between  
16 10 microns and 145 microns, with an average particle size of  
17 between 20 microns and 45 microns. This is because the powder

1 in the selective laser sintering machine is moved by a counter-  
2 rotating roller, and this method of powder transfer does not  
3 work well for finer powders.

4 In mixing the particles, the recommended molybdenum, wax,  
5 and phenolic thermoset resin mixture is 3% phenolic thermoset  
6 resin particles, 2.5% wax particles, balance molybdenum  
7 particles, by weight. The proper ratio of wax, phenolic  
8 thermoset resin particles, and molybdenum particles has an  
9 effect on shrinkage during selective laser sintering of the  
10 particle mixture to "tack" together the molybdenum particles and  
11 during sintering of the desired form which vaporizes the wax and  
12 phenolic thermoset resin and sinters the molybdenum particles.

13 Where mass production of simple shaped parts is desired,  
14 "cold pressing" the mixture of molybdenum particles, wax  
15 particles, and phenolic thermoset resin particles is the  
16 preferred method of shaping a desired form.

17 A version of "rapid prototyping" is preferred where the  
18 part to be manufactured is of complex or varying topography or  
19 where limited numbers of parts are to be manufactured. "Rapid  
20 prototyping" is a known technology to facilitate rapid product  
21 development. The version of rapid prototyping as disclosed  
22 herein is suitable for processing or shaping a mixture of  
23 molybdenum particles, wax particles, and phenolic thermoset

1 resin particles into a desired form. This is particularly  
2 advantageous for complex or varying topographies.

3 In rapid prototyping, a 3-D model produced on a computer-  
4 aided design (CAD) system is mathematically divided into a large  
5 number of thin layers, a few thousandths of an inch thick. The  
6 different processes for rapid prototyping generally work on the  
7 same basis principle, i.e., the desired part is built up in  
8 small layers, about 0.003" thick to about 0.005" thick, one  
9 layer at a time, starting from the bottom and working up until  
10 the entire part is finished. Thus, the layers are built, and  
11 simultaneously consolidated to the preceding layer, using the  
12 description of that layer from the computer.

13 The preferred rapid prototyping technique is "selective  
14 laser sintering" ("SLS"). SLS uses a CO<sub>2</sub> laser to sinter a  
15 mixture of molybdenum particles, wax particles, and phenolic  
16 thermoset resin particles by scanning in the horizontal plane  
17 only as dictated by a current layer description in a CAD model.  
18 The three dimensional solid is built up by the addition of  
19 material layers.

20 The SLS machine consists of hardware and software  
21 components. The hardware components include the process chamber  
22 and powder engine, the controls cabinet, and the atmospheric  
23 control unit. The process chamber incorporates the laser, pre-  
24 heater, and the powder handling equipment. The controls cabinet

1 interprets the CAD drawing and controls and monitors the SLS  
2 process. The atmospheric control unit regulates the temperature  
3 and amount of N<sub>2</sub> flowing through the air in the chamber. It also  
4 filters the air that flows through the process chamber. The  
5 software components utilize the UNIX operating system and other  
6 DTM Corporation proprietary applications.

7 The CAD drawing is geometrically modified to horizontally  
8 divide the desired form into thin horizontal layers. These  
9 layers can be adjusted in thickness, but are typically about  
10 0.003" to about 0.005" in thickness. The thin layers represent  
11 sintering planes to be traced by the CO<sub>2</sub> laser. In operation, a  
12 layer of a mixture of molybdenum particles, wax particles, and  
13 phenolic thermoset resin particles is spread out. When the  
14 desired cross section of the layer is traced out by the CO<sub>2</sub>  
15 laser, the temperature of the mixture of molybdenum particles,  
16 wax particles, and phenolic thermoset resin particles is  
17 increased, and the wax and phenolic thermoset resin particles  
18 fuse the molybdenum particles together. The part is then  
19 lowered in the SLS machine by 0.003" to 0.005" (depending upon  
20 the layer thickness), and new layers are added in a similar  
21 fashion to form the solid mass. The SLS machine builds the part  
22 one layer at a time by creating the bottom layer first, and then  
23 adding layers until the part is finished.

1       The mixture of molybdenum particles, wax particles, and  
2 phenolic thermoset resin particles was laser sintered using the  
3 DTM SINTERSTATION 2500plus machine which sinters only the wax  
4 and phenolic thermoset resin particles and not the molybdenum  
5 particles. As described below, post processing is necessary to  
6 vaporize, sublime, or "burn off" the wax and phenolic thermoset  
7 resin and sinter the molybdenum particles. After this, the  
8 sintered molybdenum substrate, which is porous, is infiltrated  
9 with an oxygen free copper. This post-SLS processing generally  
10 results in a small shrinkage due to the vaporization of the wax  
11 and phenolic thermoset resin and sintering of the molybdenum  
12 particles. By holding the processing variable constant, this  
13 shrinkage may be compensated for in the CAD design of the part,  
14 i.e., the CAD design provides for a slightly larger molybdenum,  
15 wax, and phenolic shaped form, such that upon shrinkage, the  
16 molybdenum-copper composite part will be the desired size.

17       The CO<sub>2</sub> laser used in the SLS machine is generally only  
18 capable of producing enough heat to fuse low-melting thermoset  
19 synthetic resin such as phenolic; as such, it is these and  
20 similar low-melting point materials, such as wax, which are used  
21 to mix with the molybdenum particles when the SLS process is  
22 employed. Additionally, the wax and phenolic thermoset resin  
23 used must suitably vaporize or sublime in the vaporization step  
24 prior to sintering the molybdenum particles.

1       The desired parameters for SLS shaping of a mixture of  
2 molybdenum particles, wax particles, and phenolic thermoset  
3 resin particles to the desired form are as follows:

4       Layer thickness: 0.003 inches

5       Right and left feed heater temperature: 55 degrees C

6       Part heater set point: 75 degrees C

7       Laser power: 12 Watts

8       Scan spacing: 0.003 inches

9       Scan speed: 150 inches per second

10       After sintering or cold pressing has been completed, the  
11 green form is placed on an aluminum oxide plate which is located  
12 in a graphite crucible. Oxygen free copper is placed on top of  
13 tabs, which are also formed from the molybdenum, phenolic, wax  
14 mixture, that are adjacent to the green form. The amount of  
15 oxygen free copper to be used is  $0.72 \times$  green weight including  
16 the green form and the tabs. The oxygen free copper is placed  
17 on the tabs and the entire green form, tabs, and oxygen free  
18 copper infiltrant material is then covered with aluminum oxide  
19 in particulate form. The crucible is then placed in a furnace  
20 with a process gas of 5% hydrogen, balance argon, and a process  
21 pressure of 1 Torr. The green form material and the oxygen free  
22 copper are subjected to a furnace cycle. The furnace cycle  
23 comprises taking the green form material and the oxygen free  
24 copper from room temperature (approximately 68 degrees

1 Fahrenheit) to 600 degrees Centigrade over a period of 3 hours,  
2 holding at 600 degrees Centigrade for 1 hour, heating from 600  
3 degrees Centigrade to 1,150 degrees Centigrade over a period of  
4 2.3 hours, holding at 1,150 degrees Centigrade for 0.5 hours,  
5 then reducing the temperature from 1,150 degrees Centigrade to  
6 room temperature over a time period of 3 hours. During this  
7 single furnace cycle, vaporization of the wax and phenolic  
8 binder, sintering of the molybdenum particulate, and  
9 infiltration of the sintered molybdenum particles with oxygen  
10 free copper are accomplished. The vaporization step may be  
11 referred to by those skilled in the art as "burn-out"; however,  
12 this terminology is somewhat misleading in that it is preferred  
13 that substantially no oxygen be present during the sintering  
14 step. Oxygen present in the sintering step may lead to reduced  
15 wetting in the copper infiltration step.

16 Vaporization and sintering produces a sintered molybdenum  
17 shaped form that is about 35 volume % to about 65 volume %  
18 occupied by sintered molybdenum, i.e., about 35% to about 65%  
19 dense. The density may advantageously be varied, within these  
20 limits, depending upon the desired application. The density or  
21 porosity may be altered by varying the size or size distribution  
22 of the molybdenum particles used, varying the size or size  
23 distribution of either the wax or phenolic thermoset resin  
24 particles used, varying the particle mixture ratio used, and/or

1 varying the manufacturing technique, etc. The density or  
2 porosity determines the molybdenum-copper ratio and may be  
3 optimized to meet specific objectives.

4 During the furnace operation the oxygen free copper is  
5 heated above its melting point (1,083 degrees C), such that by  
6 capillary action, the copper infiltrates into the open area of  
7 the sintered molybdenum particles to produce the molybdenum-  
8 copper composite in the desired form with an about 100% density.  
9 The resulting mixture is a molybdenum-copper composite with a  
10 volume fraction of molybdenum of between 35% and 65% with the  
11 balance oxygen free copper.

12 Generally, the resulting average particle size diameter of  
13 the composite material is 2.31 microns, the mean free path is  
14 1.99 microns, and the mean center to center particle spacing is  
15 4.61 microns.

16 The composite material of the present invention is unique  
17 in that it offers the ability to create tools and prototype  
18 parts requiring working temperatures up to 1000 degrees  
19 Centigrade. The material is also advantageous because it has a  
20 low coefficient of thermal expansion. The present invention is  
21 also unique in that it offers properties above and beyond that  
22 of the commercially available selective laser sintering material  
23 systems. For example, it has a higher thermal conductivity than  
24 known stainless steel-copper alloy composite materials. Since

1 an oxygen free copper (99.9% pure copper) is used in the preset  
2 invention it will have better thermal conductivity than known  
3 90% copper - 10% tin bronze infiltrant materials. A wide  
4 variety of parts may be made from the composite material of the  
5 present invention and the method of the present invention.

6 It is apparent that there has been provided in accordance  
7 with the present invention a molybdenum-copper composite  
8 material which fully satisfies the objects, means, and  
9 advantages set forth hereinbefore. While the present invention  
10 has been described in the context of specific embodiments  
11 thereof, other alternatives, modifications, and variations will  
12 become apparent to those skilled in the art having read the  
13 foregoing description. Accordingly, it is intended to embrace  
14 those alternatives, modifications, and variations as fall within  
15 the broad scope of the appended claims.